Optical Mixing Due to Nonlinearities Associated with the Carrier-Momentum Relaxation Time in a Magnetic Field in Semiconductors*

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The optical mixing due to nonlinearities which originate from momentum relaxation in a dc magnetic field has been developed and compared with those arising due to nonparabolic bands of charge carriers.

A great deal of attention has been paid recently to the study of optical nonlinearities in semiconductors. Patel *et al.*[1] have observed mixing of two laser beams of frequency ω_1 and ω_2 leading to generation of an output at frequency $\omega_3 = 2\omega_1 - \omega_2$, in n-InSb. There are two types of mechanisms which may be responsible for the observed optical mixing. One of the mechanisms is due to the nonparabolicity of the conduction band of the semiconductors as suggested by Wolf and Pearson,[2] who have given a semiclassical treatment of the problem. Another possible mechanism arises from nonlinearities associated with the energy dependence of the carrier-momentum relaxation time developed by Kaw[3] and Krishnamurthy and Paranjape (KP)[4] following the semiclassical approach in the warm-electron approximation.

Recently, Bierig, Weiler, and Lax (BWL)[5] have examined the effect of a dc magnetic field on nonlinear mixing in semiconductors, both experimentally and theoretically, taking into account the nonparabolicity of the conduction band. In an earlier treatment by Lax, Zawadzki, and Weiler,[6] the neglect of the momentum relaxation time in the momentum equation of motion has led to the prediction of a strong enhancement of the output as the cyclotron frequency ω_c approached ω_3, ω_2, or ω_1. Experimentally, BWL were not able to observe any cyclotron enhancement, and their explanation lies in the inclusions of magnetic-field-dependent (τ decreasing with the magnetic field) momentum relaxation time in the equation of motion. BWL's theory does not take into account the second nonlinear mechanism of optical mixing due to KP. Such a nonlinear contribution to optical mixing originating from relaxations, due to KP, may be important in certain semiconductors. It is the aim of the present communication to investigate the magnetic-field dependence of the magnitude of the third-order current density arising from this mechanism and to compare it with the work of BWL.

In order to calculate the third-order current density, we utilize the hydrodynamic equation of motion and the warm-electron approximation. Following KP, we write the equation of motion for an average carrier in an external magnetic field H as

$$\frac{\partial \vec{V}}{\partial t} + \frac{\vec{V}}{\tau(\bar{\epsilon})} = \frac{-e\vec{E}}{m} - \vec{V}\times\vec{\omega}_c , \tag{1}$$

where

$$\vec{E} = \vec{E}_1 e^{i\omega_1 t} + \vec{E}_2 e^{i\omega_2 t} + (\text{complex conjugate})$$

is the laser electric field, $\vec{V}$ is the carrier-drift velocity, $\omega_c = eH/mc$ is the cyclotron frequency of the charge carrier, m is the electronic effective mass, and $\tau(\bar{\epsilon})$ is the carrier-momentum relaxation which is regarded as a function of the average energy $\bar{\epsilon}$ of the carrier. In the presence of an intense laser beam, we can express the average energy $\bar{\epsilon}$ in the warm-electron approximation as the sum of thermal and drift energies given by

$$\bar{\epsilon}(t) = \tfrac{3}{2}\kappa T_e + \tfrac{1}{2} m V^2, \tag{2}$$

where T_e is the electron temperature. Now with the help of Eq. (2) we may write

$$\frac{1}{\tau(\bar{\epsilon})} = \frac{1}{\tau_0(\bar{\epsilon}/\kappa T)^n} \simeq \frac{1}{\tau_0}\left\{1 - \frac{n}{2}\left[\left(\frac{T_e}{T} - 1\right) + \frac{mV^2}{3\kappa T}\right]\right\}, \tag{3}$$

where T is the lattice temperature and n is an integer characterizing the type of scattering mechanism. In order to find the electron temperature T_e, we may utilize the energy-balance equation

$$\frac{d\bar{\epsilon}}{dt} = -e\vec{V}\cdot\vec{E} , \tag{4}$$

where we have neglected the energy loss of the electrons to the lattice. This is a valid assumption, provided the laser frequencies of interest satisfy the condition $\omega\tau_e \gg 1$, where τ_e is the energy relaxation time.

In proceeding further, we develop $\vec{V}$ and T_e as a sum of components of frequencies ω_1, ω_2, $2\omega_1$, etc. Substituting Eq. (3) in Eq. (1), we obtain the velocity components

$$V_x(\omega_1) = \frac{-e\Omega_1 E_{1x}}{m(\Omega_1^2 + \omega_c^2)}, \quad V_x^*(\omega_2) = \frac{-e\Omega_2 E_{2x}^*}{m(\Omega_2^2 + \omega_c^2)},$$

$$V_y(\omega_1)=\frac{-e\omega_c E_{1x}}{m(\Omega_1^2+\omega_c^2)},\quad V_y^*(\omega_2)=\frac{-e\omega_c E_{2x}^*}{m(\Omega_2^2+\omega_c^2)},\tag{5}$$

and

$$V_z(\omega_1)=V_z(\omega_2)=0,$$

where $\Omega_1=(i\omega_1\tau_0+1)/\tau_0$ and $\Omega_2=(-i\omega_2\tau_0+1)/\tau_0$. In arriving at Eq. (5), we have taken the laser field $\vec{E}$ along the x direction and the applied dc magnetic field along the z direction. The third-order current density may be expressed using Eqs. (3) and (1) as

$$J_{3xp}=-NeV_{3xp}(\omega_3)=-\frac{n}{2}\,\frac{Ne^2}{\tau_0 m\kappa T}\,\frac{1}{\Omega_3^2+\omega_c^2}\left(E_{1x}\,\frac{\omega_c^2-\Omega_3\Omega_1}{\Omega_1^2+\omega_c^2}\,[\kappa T_e(\omega_1-\omega_2)+\tfrac{2}{3}m\vec{V}(\omega_1)\cdot\vec{V}^*(\omega_2)]\right.$$
$$\left.+E_x^*\,\frac{\omega_c^2-\Omega_3\Omega_2}{\Omega_2^2+\omega_c^2}\,[\kappa T_e(2\omega_1)+\tfrac{1}{3}mV^2(\omega_1)]\right),\tag{6}$$

where $\Omega_3=(i\omega_3\tau_0+1)/\tau_0$, and N is the carrier concentration. The subscript p refers to the parabolic case under consideration. In order to simplify Eq. (5), we need to know $\kappa T_e(2\omega_1)$ and $\kappa T_e(\omega_1-\omega_2)$ which may be obtained by combining Eqs. (2) and (4):

$$\kappa T_e(2\omega_1)=\frac{-ie^2E_{1x}^2}{3m(\omega_1\tau_0)(\Omega_1^2+\omega_c^2)},\tag{7}$$

$$\kappa T_e(\omega_1-\omega_2)=\frac{2ie^2E_{1x}E_{2x}^*}{3m(\omega_1-\omega_2)(\Omega_1^2+\omega_c^2)(\Omega_2^2+\omega_c^2)}\times[i(\omega_1-\omega_2)(\omega_c^2+\Omega_1\Omega_2)-\Omega_2(\Omega_1^2+\omega_c^2)-\Omega_1(\Omega_2^2+\omega_c^2)]\,.\tag{8}$$

Now utilizing Eqs. (5), (7), and (8) in Eq. (6), we get

$$J_{3xp}=-\frac{nNe^4E_{1x}^2E_{2x}^*}{6\kappa Tm^2\tau_0}[(L_1L_2-M_1M_2\tau_0^{-2})+i\tau_0^{-1}(L_1M_2+L_2M_1)][(\omega_1^2-\omega_c^2)^2+4\omega_1^2\tau_0^{-2}]^{-2}\times[(\omega_2^2-\omega_c^2)^2+4\omega_2^2\tau_0^{-2}]^{-1}[(\omega_3^2-\omega_c^2)^2+4\omega_3^2\tau_0^{-2}]^{-1},\tag{9}$$

where

$$L_1=(\omega_1^2-\omega_c^2)^2(\omega_2^2-\omega_c^2)(\omega_3^2-\omega_c^2)-8\omega_1(\omega_1^2-\omega_c^2)(\omega_2\omega_3+\omega^2)(\omega_2-\omega_3)\tau_0^{-2},$$

$$L_2=2\,[\omega_c^4+\omega_c^2\omega_1(\omega_2+\omega_3)+\omega_1^2\omega_2\omega_3]+[(\omega_2\omega_3-\omega_c^2)(\omega_1^2-\omega_c^2)]$$
$$+(1/\omega_1)[\omega_1^2-\omega_c^2)(\omega_3-\omega_2)-2\omega_1(\omega_3\omega_2-\omega_c^2)]\tau_0^{-2}-[4/(\omega_1-\omega_2)][(\omega_1+\omega_3)(\omega_1\omega_2+\omega_c^2)]\tau_0^{-2},$$

$$M_1=2[(\omega_1^2-\omega_c^2)^2(\omega_2\omega_3+\omega_c^2)(\omega_2-\omega_3)+2\omega_1(\omega_1^2-\omega_c^2)(\omega_2^2-\omega_c^2)(\omega_3^2-\omega_c^2)],$$

and

$$M_2=2[\omega_1\omega_3(\omega_1-\omega_2)-\omega_1\omega_2(\omega_1+\omega_3)-\omega_c^2(\omega_2+\omega_3)]+[(\omega_1^2-\omega_c^2)(\omega_3-\omega_2)-2\omega_1(\omega_2\omega_3-\omega_c^2)]-(1/\omega_1)[(\omega_2\omega_3-\omega_c^2)(\omega_1^2-\omega_c^2)]-4/(\omega_1-\omega_2)[(\omega_1\omega_3+\omega_c^2)(\omega_1\omega_2+\omega_c^2)].\tag{10}$$

Equation (9) is the basic result of the present investigation. In the situation where $H=0$, i.e., $\omega_c=0$, Eq. (9) takes the form

$$J_{3xp}^0=\frac{n}{2}\,\frac{Ne^4E_{1x}^2F_{2x}^*}{m^2\kappa T\omega_1\omega_2\omega_3}\left(-\frac{1}{\omega_1\tau_0}+i\,\frac{A}{(\omega_1\tau_0)^2}\right),\tag{11}$$

which is in agreement with the results of KP [see Eq. (11) of KP]. In the foregoing expression[7]

$$A=\frac{6\omega_1^3-5\omega_2^3-14\omega_1^2\omega_2+17\omega_1\omega_2^2}{3(\omega_1-\omega_2)},\tag{12}$$

where we have assumed that $\omega\tau_0\gg1$ and retained terms up to $1/(\omega\tau_0)^2$ for the frequency range of interest.

We may write the magnitude of the third-order current density ratio,

$$R_1=|J_{3xp}|/|J_{3xp}^0|=\omega_1^8\omega_2^4\omega_3^4\,\frac{(L_1L_2-M_1M_1\tau_0^{-2})^2+\tau_0^{-2}(L_1M_2+L_2M_1)^2}{(L_1^0L_2^0-M_1^0M_2^0\tau_0^{-2})^2+\tau_0^{-2}(L_1^0M_2^0+L_2^0M_1^0)^2}\times[(\omega_1^2-\omega_c^2)^2+4\omega_1^2\tau_0^{-2}]^{-2}[(\omega_2^2-\omega_c^2)^2+4\omega_2^2\tau_0^{-2}]^{-1}[(\omega_3^2-\omega_c^2)^2+4\omega_3^2\tau_0^{-2}]^{-1},\tag{13}$$

where L_1^0, L_2^0, M_1^0, and M_2^0 are, respectively, the quantities L_1, L_2, M_1, and M_2 when $H=0$.

We shall consider the nonlinear case of nonparabolic origin for the third-order current density in a magnetic field developed by BWL and write [from Eq. (3) of BWL]

$$J_{3xNP}=\frac{Ne^4\omega_3E_{1x}^2E_{2x}^*[-\tau_0^{-1}(A_1B_2+A_2B_1)+i(A_1A_2-B_1B_2\tau_0^{-2})]}{m^2\epsilon_g[(\omega_1^2-\omega_c^2)^2+4\omega_1^2\tau_0^{-2}][(\omega_2^2-\omega_c^2)^2+4\omega_2^2\tau_0^{-2}][(\omega_3^2-\omega_c^2)^2+4\omega_3^2\tau_0^{-2}]},\tag{14}$$

where ϵ_g is the energy gap of the semiconductor,

$$A_1 = [(\omega_1^2 - \omega_c^2)^2(\omega_2^2 - \omega_c^2)(\omega_3^2 - \omega_c^2) - 8\omega_1(\omega_1^2 - \omega_c^2)(\omega_2\omega_3 + \omega_c^2)(\omega_2 - \omega_3)\tau_0^{-2},$$

$$A_2 = 3\omega_c^4 - \omega_c^2(\omega_1^2 + \omega_2\omega_3 - 2\omega_1\omega_2 - 2\omega_1\omega_3) + 3\omega_1^2\omega_2\omega_3 ,$$

$$B_1 = 4\omega_1(\omega_1^2 - \omega_c^2)(\omega_2^2 - \omega_c^2)(\omega_3^2 - \omega_c^2) + 2(\omega_2 - \omega_3)(\omega_1^2 - \omega_c^2)^2(\omega_2\omega_3 + \omega_c^2) ,$$

$$B_2 = (\omega_1^2 - \omega_c^2)(\omega_3 - \omega_2) - 2\omega_1(\omega_2\omega_3 - \omega_c^2) + 2(\omega_1 - \omega_2)(\omega_1\omega_3 + \omega_c^2) - 2(\omega_1 + \omega_3)(\omega_1\omega_2 + \omega_c^2) , \quad (15)$$

and the subscript NP refers to the nonparabolic case.

In arriving at Eq. (14), we have taken $\vec{E}$ along the x direction and $\vec{H}$ along the z direction for the purpose of comparison with Eq. (9).

The ratio of the magnitude of the current from Eq. (14) may be expressed as

$$R_2 = |J_{3xNP}|/|J^0_{3xNP}| = \frac{\omega_1^8\omega_2^4\omega_3^4[\tau_0^{-2}(A_1B_2 + A_2B_1)^2 + (A_1A_2 - B_1B_2\tau_0^{-2})^2]^{1/2}}{[(\omega_1^2 - \omega_c^2)^2 + 4\omega_1^2\tau_0^{-2}][(\omega_2^2 - \omega_c^2)^2 + 4\omega_2^2\tau_0^{-2}]}$$

$$\times \frac{[\tau_0^{-2}(A_1^0B_2^0 + A_2^0B_1^0)^2 + (A_1^0A_2^0 - B_1^0B_2^0\tau_0^{-2})^2]^{-1/2}}{(\omega_3^2 - \omega_c^2)^2 + 4\omega_3^2\tau_0^{-2}} , \quad (16)$$

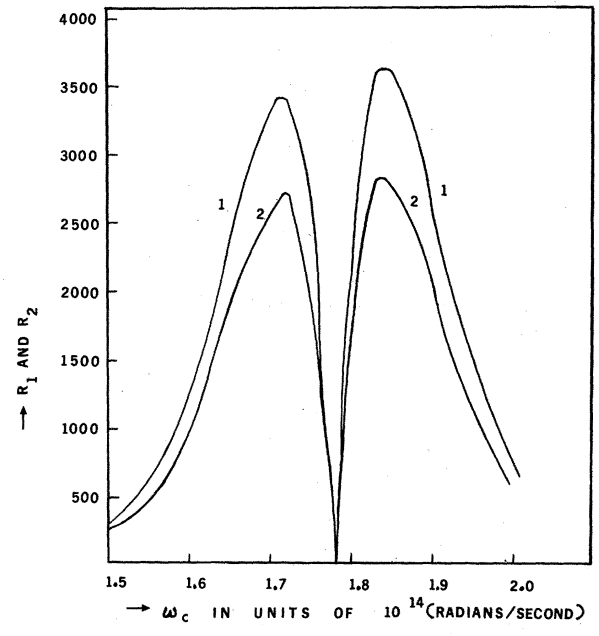

FIG. 1. Plot of third-order (mixing) current density ratios R_1 and R_2 vs cyclotron frequency for the following values of the parameters: $\omega_1 = 1.78 \times 10^{14}$ rad/sec, $\omega_2 = 1.96 \times 10^{14}$ rad/sec, and $\omega_3 = 159 \times 10^{14}$ rad/sec, and $\tau_0 = 10^{-14}$ sec. Curve 1 : R_1 vs ω_c rad/sec and corresponds to the nonlinear mechanism due to KP. Curve 2 : R_2 vs ω_c rad/sec and corresponds to the nonlinear mechanicsm due to BWL.

where J^0_{3xNP}, A_1^0, A_2^0, B_1^0, and B_2^0 are, respectively, J_{3xNP}, A_1, A_2, B_1, and B_2, when $\vec{H} = 0$. We have estimated numerically the values of R_1 and R_2 for various values of ω_c, ranging between $\omega_c = 0$ and $\omega_c = 2 \times 10^{14}$ rad/sec for the following parameter values: $\omega_1 = 1.78 \times 10^{14}$ rad/sec (10.6-μ radiation), $\omega_2 = 1.96 \times 10^{14}$ rad/sec (9.6-μ radiation), $\omega_3 = 1.59 \times 10^{14}$ rad/sec (11.8-μ radiation), and $\tau_0 = 10^{-13}$ sec. It is found that both R_1 and R_2 increase with ω_c up to $\omega_c = 1.72 \times 10^{14}$ rad/sec and decrease drastically and go to zero when $\omega_c = \omega_1 = 1.78 \times 10^{14}$ rad/sec (see Fig. 1). It can be seen from Eqs. (13) and (16) also that $R_1 = R_2 = 0$ when $\omega_c = \omega_1$. For $\omega_c > \omega_1$, R_1 and R_2 increase and reach a maximum value when $\omega_c = 1.84 \times 10^{14}$ rad/sec and decrease again. Further, it is interesting to note that $R_1 \geq R_2$ for low magnetic field ($\omega_c \ll \omega_{1,2,3}$) and $R_1 > R_2$ for magnetic fields such that $\omega_c \lesssim \omega_{1,2,3}$. It should be noted that R_1 and R_2 just describe the magnetic-field dependence of the magnitudes of the current densities of the two nonlinear mechanisms under consideration. The relative magnitude of the two nonlinear mechanisms may be expressed in terms of the ratio

$$R = \frac{|J_{3xp}|}{|J_{3xNP}|} = \frac{|J^0_{3xp}|}{|J^0_{3xNP}|}\frac{R_1}{R_2} \simeq \frac{n}{6}\frac{\epsilon_g}{\kappa T}\frac{1}{\omega_3\tau_0}\frac{R_1}{R_2} , \quad (17)$$

where we have assumed $\omega\tau_0 \gg 1$.

We may observe from Eq. (17) that the ratio R is of the order of unity for InSb ($\epsilon_g/\kappa T = 33$ at $T = 80\,^\circ$K, $n = 3$ for dominant impurity scattering and $\omega_3\tau_0 = 15.9$). For low temperatures, however, R could exceed beyond unity in which case the nonlinear mechanism due to KP is more important than the mechanism due to BWL. Of course, for a purely parabolic semiconductor, the contribution from a BWL mechanism will be zero, while relaxational nonlinearity would be the only operational nonlinear mechanism. Experiments on semiconductors with almost parabolic energy bands may confirm the predictions of our theory.

It has been generally accepted that nonlinear mixing in semiconductors could arise from nonparabolicity of the conduction band. Even though this conclusion is correct for nonparabolic semiconductors, there is a tendency to extend this result to semiconductors in which nonparabolicity is not significant. The first calculation independent of nonparabolicity was proposed by Kaw. His model is based on the energy dependence of relaxation time of conduction electrons. The model is criticized by Wynne[8] who argues that nonlinearity is

mainly due to nonparabolicity rather than to Kaw's model. Superficially it could appear that results of Kaw may have insignificant contributions to nonlinearity since the conclusions are derived as a second-order effect to the electronic motion. Recent extension of Kaw's model by KP, however, shows that nonlinear mixing is a first-order effect if the laser frequency is very much greater than τ_0. If $\omega\tau_0$ is exceedingly large, as can be seen from Eq. (17), then the relative importance of nonlinearity due to BWL is greater than that due to the relaxational process. At low temperatures ($\sim 4\,^\circ$K) and with samples with large impurity concentration, it may be concluded that the relaxational contribution to nonlinearity may exceed the contribution from nonparabolicity.

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[1]C. K. N. Patel, R. E. Slusher, and P. A. Fleury, Phys. Rev. Letters 17, 1011 (1966).

[2]P. A. Wolf and G. A. Pearson, Phys. Rev. Letters 17, 1015 (1966).

[3]P. Kaw, Phys, Rev. Letters 21, 539 (1968).

[4]B. S. Krishnamurthy and V. V. Paranjape, Phys. Rev. 181, 1153 (1969).

[5]R. W. Bierig, M. H. Weiler, and B. Lax, Phys. Rev. 186, 747 (1969).

[6]B. Lax, W. Zawadzki, and M. H. Weiler, Phys. Rev. Letters 18, 462 (1967).

[7]In the earlier work (KP), there was, unfortunately, numerical error in the expression for A.

[8]J. J. Wynne, Phys. Rev. 178, 1295 (1969).

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Longitudinal-Optical Phonons in TiO_2 (Rutile) Thin-Film Spectra

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The infrared spectra of oxidation films on titanium show an asymmetrical absorption band at 828 cm^{-1} not found as an infrared-active mode in single-crystal TiO_2. It is identified as two superposed longitudinal-optical modes at approximately 828 and 809 cm^{-1} on the basis of optical tests and theoretical predictions.

In the course of investigating the infrared reflection spectra of polycrystalline oxidation films on titanium and titanium-based alloys, [1] one absorption band is found at 828 cm^{-1} which is not identifiable with infrared-active modes of rutile reported in the literature. Figure 1 shows typical reflection spectra of two such films in p-polarized radiation at 15° angle of incidence, obtained on a PE No. 225 grating spectrophotometer with a wire grid polarizer. The starting material was RMI 30 titanium sheet electropolished to a mirror finish and then oxidized in the temperature range 500–825 °C in a 0.2 O_2/0.8 Ar atmosphere for various periods of time up to 16 h. The $\frac{1}{2}$-h spectrum is typical of those of the thinner films, showing channel spectra in the region of transparency and absorption bands below 1000 cm^{-1}. The 2-h spectrum approaches that of the single-crystal rutile where the reststrahlen structure is prominent including the reflection minima around 870 cm^{-1}. Only rutile is detected in these films by x-ray diffraction.

The bands at 470 and 370 cm^{-1} are clearly identified with two of the ordinary-ray E_u modes reported by Spitzer *et al.*[2] in the single crystal. Another single-crystal study by Liebisch and Rubens,[3] however, is in error. They find no band around 370 cm^{-1} in the ordinary ray but instead one at 408 cm^{-1} in the extraordinary ray. (Spitzer's results were confirmed with a natural rutile crystal in this laboratory.) Both references report weak broad reflection minima around 670 and 570 cm^{-1} which are also observed in many of these thin-film spectra. Neither indicates any bands present around 828 cm^{-1}.

The 828 -cm^{-1} band is believed to be two superposed longitudinal-optical (LO) modes of rutile for the following reasons:

(1) The band appears only in the thinner films and is not present in the thicker films in which the reststrahlen structure becomes prominent.

(2) It is present only in p-polarized radiation.

(3) It is more intense at 32° than at 15° angle of incidence. These properties, cited by Berreman[4] as characteristics of LO-mode absorption bands, are illustrated in Fig. 2.

With the aid of an analog curve resolver, it is possible to find two Gaussian components in this